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Removal Of Metals From Electroplating Wastes Using Neem Bark

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Abstract: Neem bark *(Azadirachta indica A. Juss.)* was investigated for its effectiveness in adsorbing metal ions from electroplating waste and synthetic solutions, both in batch and continuous-flow experiments. The sorption process was influenced by both pH and concentration, with an optimal pH range of 4 to 5. The equilibrium data were consistent with the Langmuir isotherm model, showing maximum adsorption capacities of 8.48 mg/g for Cu in electroplating waste and 13 to 46 mg/g in synthetic solutions. Competitive studies revealed the metal sorption affinity followed the order: Cu(II) > Cr(III) > Zn(II). In continuous-flow experiments, breakthrough curves for Cu(II) and Zn(II) from electroplating waste were obtained at varying bed depths and flow rates, with Cu(II) showing a higher sorption efficiency on Neem bark powder compared to Zn(II).

Index terms - Sorption, neem bark powder, electroplating waste, Cu(II), Zn(II).

I. INTRODUCTION

The removal of heavy metals from aqueous solutions can be accomplished through various methods, including ion exchange, chemical precipitation, membrane filtration, and coagulation with alum or iron. Among these, adsorption is a widely practiced technique, particularly using activated carbon, which is effective at removing trace levels of heavy metals (Huang & Blankenship, 1984). However, the high cost of activated carbon has driven research into more affordable alternatives. In recent years, low-cost materials have been explored as substitutes (Pollards et al., 1992). Biosorbents, which are abundant and easily obtainable, have gained significant attention for metal removal. For instance, modified groundnut (Arachis hypogea) treated with ethylenediamine tetraacetic acid (EDTA) has been used to remove copper (Cu) and Zinc (Zn) ions (Okiemen et al., 1991). Additionally, Rao and colleagues (1992) studied the sorption of chromium (Cr) using coconut-shell carbon. Other biological materials found effective in metal removal from aqueous systems include polymerized corncob (Henderson et al., 1977), moss (Low & Lee, 1987), hulls and bran (Marshall et al., 1993), and water hyacinth roots (Low et al., 1994). This paper explores the potential of Neem bark powder as a biosorbent for the removal of copper (Cu(II)) and Zinc (Zn(II)) from electroplating wastes and synthetic solutions.

II. MATERIALS AND METHODS

2.1 Properties of Neem Barks

Properties of Neem bark is essential for understanding the various characteristics of the adsorbents developed from neem bark. This phenomenon is crucial when a novel material is designed to remove specific contaminants. The six developed adsorbents (NB-A1 to NB-A6) are characterized adopting Fourier Transform Infrared (FTIR) Spectroscopy (Frontier, Perkin Elmer), performed in the range of 4000 to 400 cm, to analyze the vibration modes of the functional groups present. Among these, the adsorbent with the relevant functional groups on its surface and the highest adsorption capacity for removing Cr(VI), Cu(II), and Zn(II) is selected in the current study and termed as nNB-A.

2.2 Preparation of Stock Solution

To prepare the 1000 mg/L stock solutions, a specific amount of each metal complex salt is dissolved in distilled water, and the final volume is adjusted to 1000 ml. The precise amounts of salts used as per Standard Method in APHA (2002). All chemicals adopted in this study are of Analytical Reagent. To prepare 1000ppm stock solution using different salts with their respective quantity and molecular weight of the salts.

III. BATCH STUDIES

3.1 Effect of pH

The influence of pH on metal sorption was investigated by equilibrating sorption mixtures at various initial pH levels. This was achieved by adjusting the pH with 0.1 M HCl or NaOH before adding a pre-weighed amount of sorbent. The sorption mixtures comprised 0.1 g of banana pith in 25 ml of synthetic solution, or 10 ml in the case of electroplating waste.

3.2 Effect of Initial Concentration

The impact of initial concentration on copper sorption by neem bark powder was examined by varying the copper concentration from 10 to 100 µg/ml in the synthetic solution, and from 10 to 78 µg/ml in the electroplating waste, both at a pH of 4.40.

3.3 Effect of Contact Time

For all contact-time experiments, the sorption mixture contained 1.0 g of neem bark powder in 400 ml of solution at a pH of 4.28. The experiments were conducted at room temperature using a gyratory shaker operating at 200 rev/min. At specified time intervals, aliquots of the solution were withdrawn and analyzed for the metal of interest.

3.4 Effect of Competing Metal Ions

The study on competing metal ions included Cu(II), Cr(III), and Zn(II). Two series of equimolar solutions with concentrations of 50 and 5000 µg/ml of these metals were used to assess their effect.

3.5 Continuous Flow

Columns with an internal diameter of 3 cm were packed with neem bark powder to heights of 5, 10, and 15 cm, corresponding to 1, 2, and 3 grams of material, respectively. The flow rate was set to 10 ml/min, and 50 ml aliquots of the solution were collected and analyzed for copper (Cu), Cromium (Cr) and nickel (Ni). The influence of flow rates on sorption was also examined by using flow rates of 5, 10, and 20 ml/min at a bed depth of 5 cm.

IV. RESULTS AND DISCUSSION

The metal sorption capacities of different biological materials are presented in Table 1. Acid-treated neem bark powder demonstrated a higher sorption capacity for Cu and Zn compared to moss, which is typically considered an efficient sorbent for various metals (Low & Lee, 1991). The lower uptake of neem bark powder could be attributed to the saturation of sorption sites by Cu, as copper exhibits a higher sorption affinity than zink. Previous studies have also noted the low affinity of Zn in other biological systems. For instance, in research on the sorption of Cu and Zn from electroplating waste using water-hyacinth roots, Zn was displaced by Cu ions when the binding sites became saturated (Low et al., 1994). Similarly, the low affinity of Zn in sludge has been explained by its high binding capacity for soluble ligands and its limited competitiveness with other metals present in the same solution (Sterritt et al., 1981). These findings suggest that neem bark powder could serve as a cost-effective material for the removal or reduction of metal ions in solution.

The impact of pH on the removal of copper from electroplating waste is illustrated in Fig. 1. The uptake percentage rose from 3.9% at pH 1.54 to 80.2% at pH 4.50, underscoring the critical role of pH control for optimal sorption. The pH of the solution affects both the metal's aqueous chemistry and the binding sites on the neem bark powder. At lower pH levels, the sorbent surface is closely associated with hydronium ions (H_3O^+), which create repulsive forces that obstruct metal access to the surface functional groups. As pH increases, more functional groups on the sorbent surface become available for metal binding. Sorption improves with increasing pH until the metal ions begin to precipitate, which occurs at pH 4.5 for electroplating waste. Similar pH effects on copper and zink removal from synthetic solutions have been observed, with copper showing a higher affinity than zink, corroborating earlier findings.

The Cu-removal efficiency of neem bark powder at different Cu concentrations at pH 4.28 is illustrated in Fig. 2. A rapid uptake occurred within the first 20 minutes, with equilibrium being reached after 45 minutes in all cases. The sorption isotherms exhibit two distinct phases: an initial rapid sorption phase lasting about 20 minutes, followed by a more gradual rise. This suggests that the sorption process may be complex, potentially involving multiple mechanisms. At equilibrium, the Cu ion uptake was 95%, 65%, and 33.5% for 10, 50, and 100 µg/ml solutions, respectively, and 55% for electroplating waste with an initial Cu(II) concentration of 16 µg/ml. The lower Cu(II) sorption in the waste is attributed to the presence of competing ions that vie for the same binding sites on the banana pith. The general sorption isotherms applicable to Cu sorption include Langmuir, Freundlich, and BET (Brunauer-Emmett-Teller) types. The Langmuir model, which assumes monolayer coverage and constant sorption energy, can be used to represent this process.

Table 1 Comparative metal sorption capacities of various biosorbents

Bio-sorbent	Removal (%)	
	Cu (II)	Zn(II)
Acid-treated neem bark powder	70.14	16.08
Alkali-treated neem bark powder	51.37	10.82
Water-treated neem bark power	45.60	13.72
Coconut husk	54.73	9.45
Mass	79.86	26.42
Activated carbon	79.00	8.43

Note: A 0.1 g sorbent was added to 20 ml of electroplating waste, with the pH adjusted to 4.40. The initial concentrations of Cu and Ni were 65-51 µg/ml and 91-55 µg/ml, respectively.

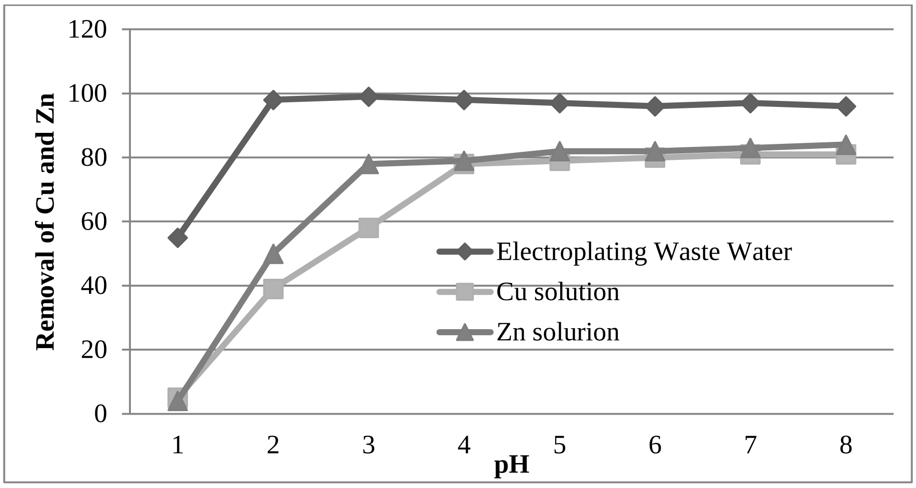

Fig 1 Effect of pH on Cu and Zn removal by neem bark powder in synthetic solutions and electroplating waste

$C_e/q_e = 1/Q_0 b + C_e/Q_0$ where Ce represents the equilibrium concentration (μg/ml), qe denotes the amount of copper sorbed at equilibrium (mg/g), Qo is the maximum sorption capacity of the neem bark powder copper system, and b is the Langmuir constant related to the energy of sorption (l/mg). By plotting Ce/qe versus Ce, the parameters for the Langmuir isotherm can be determined. Figure 3 illustrates that the experimental data for both the synthetic copper solution and copper in electroplating waste fit well with the Langmuir isotherm. This fit indicates that monolayer sorption and constant sorption energy were present under the experimental conditions. From the isotherms, the maximum sorption capacities (Qo) were estimated to be 13.46 mg/g and 8.55 mg/g for the two systems. In contrast, Marshall et al. (1993) reported a significantly lower sorption value of 1-2.1 mg/g for Cu when rice milling by-products were used as the sorbent. This difference is likely due to the presence of different binding groups in the two biological materials. However, the current study's value is only half that of the Cu-moss system reported by Lee & Low (1989). Despite its lower sorption value, banana pith's advantages include its ease of availability and abundance.

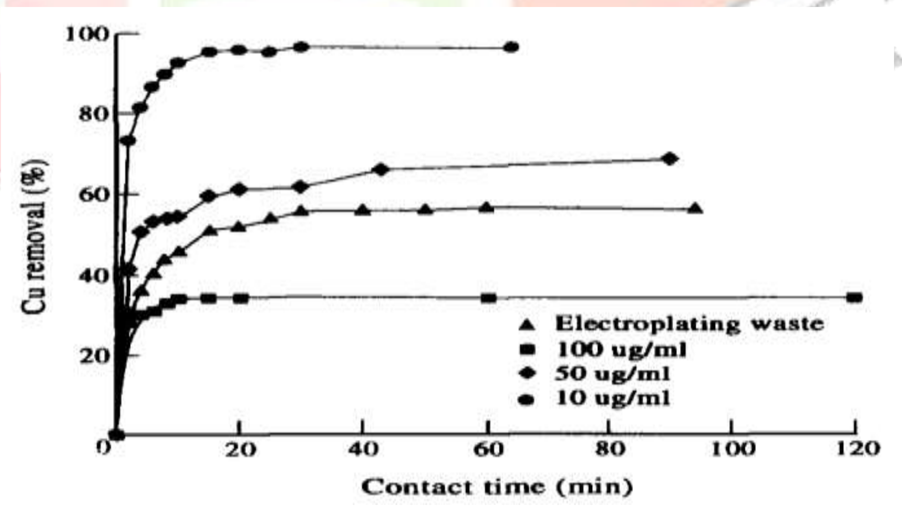

Fig 3 Removal of Cu as a function of contact time for various Cu concentrations

4.1 Effect of Competing Metal Ions on Sorption Performance:

The competitive uptake of copper in the presence of various metal ions commonly found in electroplating waste is illustrated in Table 2. The binding sites on the neem bark powder are limited, so when multiple cations (Cu, Cr, and Zn) are present in the same solution, they compete for these sites. The amount of each ion sorbed depends on the equilibrium established among the competing cations. At a low concentration (50 µM), most of the metal ions were effectively sorbed by the banana pith, as there were sufficient binding sites available. However, at a higher concentration (5000 µM), although the order of sorption remained the same, the overall percentage of sorption significantly decreased. The observed order of sorption affinity is consistent with other bio-sorbents, such as moss and water hyacinth roots (Lee & Low, 1989; Low et al., 1994), suggesting the presence of similar functional groups in these bio-sorbents.

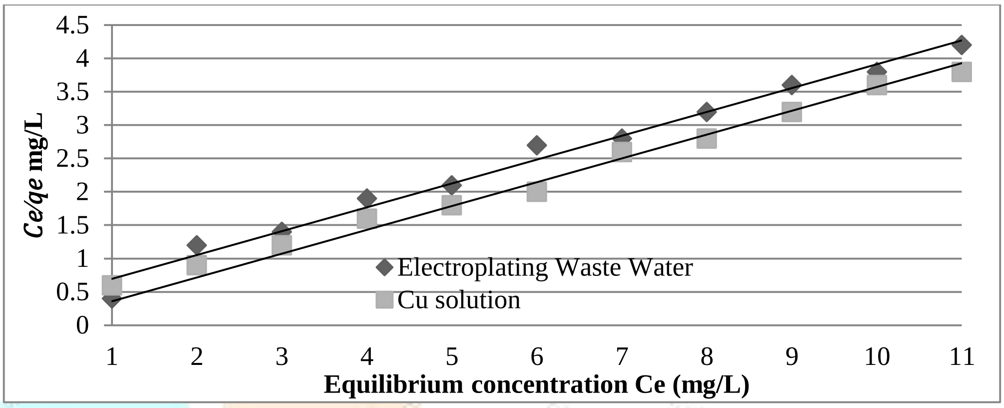

Fig. 3 Langmuir isotherms of Cu sorption on neem bark powder

Table 2 Sorption of Cu(II), Cri(II) and Zn(II) ions by neem bark powder in a mixture

Concentration	**Removal %**		
	Cu(II)	**Cr(II)**	**Zn(II)**
50 µM	96.32	82.48	90.46
5000 µM	7.24	0.58	2.61

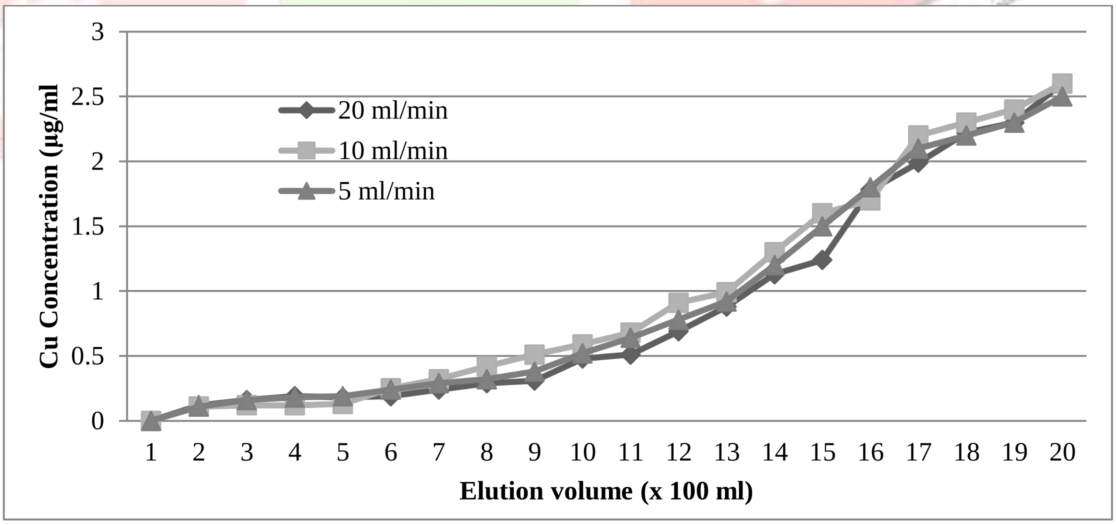

Fig. 4 The breakthrough curves of Cu from a continuous flow of electroplating waste at different bed depths

4.2 Flow Studies:

Parameters obtained from batch processes provide valuable insights into the effectiveness of metal-biosorbent systems. However, the data from these processes often do not accurately reflect conditions in flow systems, where contact times are typically too short to achieve equilibrium. Consequently, it is common to conduct column studies to better understand the system's behavior. In this study, the copper and nickel loading phase was conducted using a continuous aqueous stream of electroplating waste, containing primarily Cu (2.58 µg/ml) and Zn (6.54 µg/ml), with the solution pH adjusted to 4.4.

The resulting elution curve for Cu exhibited the characteristic 'S' shape of a packed-bed sorption system, starting with a period of minimal solute presence, followed by a gradual breakthrough that eventually reached the feed copper concentration, as depicted in Fig. 4. The breakthrough volume increased with greater column height, likely due to the increased number of binding sites on the sorbent. Notably, increasing the bed depth from 5 to 10 cm at a flow rate of 10 ml/min resulted in more than a 100% increase in breakthrough volume. However, for a fixed bed depth at different flow rates, the breakthrough volume showed little variation, as illustrated in Fig. 5.

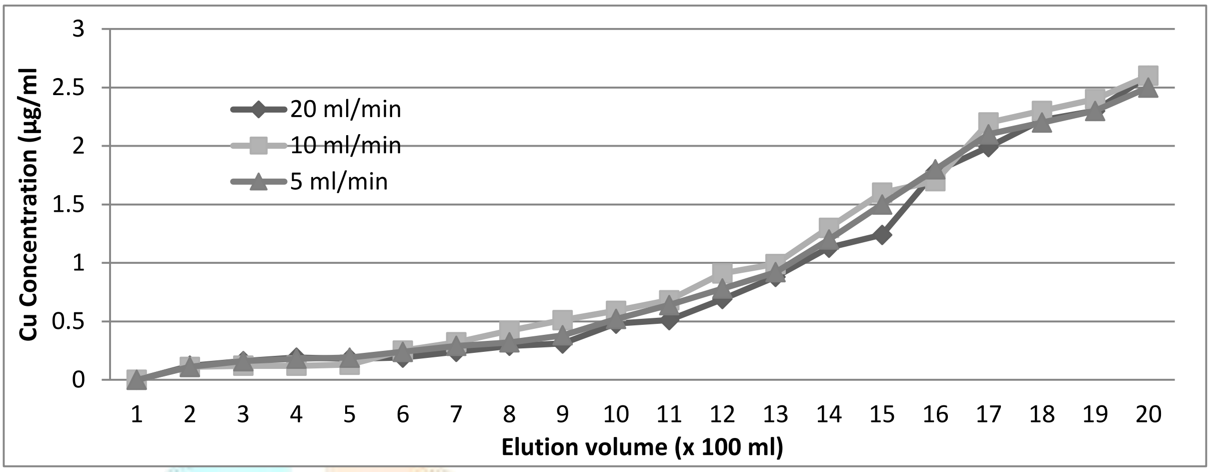

Fig. 5 Breakthrough curves of Cu at different flow rates at fixed bed depth of 5 cm

The breakthrough curves for Zn, did not follow the typical 'S' shape observed for Cu. Initially, Zn ions were adsorbed onto the sorbent, but as the eluant concentration increased, it eventually surpassed the initial concentration. This was attributed to the higher sorption affinity of Cu, which displaced Zn from the sorption sites as they became saturated. This greater sorption affinity of Cu over Zn was also evident in batch experiments and was similarly observed in flow studies involving the sorption of Cu and Zn onto non-living water hyacinth roots (Low et al., 1994).

V. CONCLUSION

Neem bark powder has proven to be an effective sorbent for copper (Cu), as demonstrated in both batch and flow studies. Copper can be easily removed from various types of electroplating wastes or from copper-salt solutions using neem bark powder. However, zink (Zn) cannot be effectively sorbed in the presence of excess copper, as copper displaces zink when the binding sites become saturated. Due to its abundant availability, neem bark powder could serve as a valuable biosorbent for the preliminary removal of copper from industrial wastewaters. Additionally, if regeneration is found to be uneconomical, the saturated material could potentially be repurposed as a source of fuel.

Acknowledgment

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